Biophysical Chemistry 140 (2009) 62–68

Contents lists available at ScienceDirect

Biophysical Chemistry

journal homepage: http://www.elsevier.com/locate/biophyschem

Medium-dependent interactions of quinones with cytosine and cytidine: A laser flash photolysis study with magnetic field effect

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ARTICLE INFO

Article history:
Received 23 October 2008
Received in revised form 19 November 2008
Accepted 21 November 2008
Available online 3 December 2008

Keywords:
9,10-anthraquinone
2-methyl 1,4-naphthoquinone
Cytosine
Cytidine
Keto-enol tautomerism
Magnetic field effect

ABSTRACT

Laser flash photolysis and an external magnetic field have been used for the study of the interaction of two quinone molecules, namely, 9,10-anthraquinone (AQ) and 2-methyl 1,4-naphthoquinone (or menadione, MQ) with a DNA base, cytosine (C) and its nucleoside cytidine (dC) in two media, a homogeneous one composed of acetonitrile/water (ACN/H_2O, 9:1, v/v) and a SDS micellar heterogeneous one. We have applied an external magnetic field for the proper identification of the transients formed during the interactions in micellar media. Cytosine exhibits electron transfer (ET) followed by hydrogen abstraction (HA) while dC reveals a reduced ET compared to C, with both quinones in organic homogeneous medium (ACN/H_2O). Due to a higher electron affinity, AQ supports more faciler ET than MQ with dC in ACN/H_2O but observations in SDS have been just the reverse. In SDS, ET from dC is completely quenched and a dominant HA is all that could be discerned. This work reveals two main findings: first, a drop in ET on addition of a ribose unit to C, which has been attributed to a role of keto-enol tautomerism in inducing ET from electron-rich nucleus and second, the effect of medium in controlling reaction mechanism by favoring HA with AQ although it is intrinsically more prone towards ET.

1. Introduction

In photosynthetic and respiratory electron transfer (ET) chains the quinones play a relevant role as mediators of vectorial electron and proton transport. The quinone molecules are localized within the biological membrane, where they form a freely diffusing "pool" component. Surfactant micelles are the simplest equivalent of biological membranes and therefore are frequently employed to mimic the biological aggregates. Hence a study of quinone molecules within micelles (SDS) and then comparing the results with that in homogeneous medium (ACN/H_2O) can be useful in obtaining insight into the reaction mechanisms and changes if any, with different biomolecules. We are currently interested in the study of changes in reactivity caused by restricted geometry conditions utilizing quinones with DNA bases [1–5]. These are conditions in which one (or both) reactant(s) is (are) forced to remain (totally or partially) at the hydrophobic core of a micelle. These studies are of interest because (i) the local concentrations of the reactants can increase or decrease in relation to their bulk values, thus allowing the tuning of reaction rates, and (ii) the properties of local and bulk media are different which implies changes in reactivity. In this regard, we have studied the interaction of two quinone molecules, menadione (2-methyl 1,4-naphthoquinone, MQ) and 9,10-anthraquinone (AQ) well-known for the anticancer activity of their derivatives with one of the pyrimidine DNA bases, cytosine (C) and its nucleoside, cytidine (dC) in two different categories of media, a homogeneous one composed of acetonitrile/water (ACN/H_2O, 9:1, v/v) and a heterogeneous micellar (sodium dodecyl sulphate, SDS) one.

Photoinduced electron transfer (PET) from DNA was established as an important reaction, responsible for DNA damage. Many works were done on quinone–DNA interactions [6–9]. Our interest in the photochemistry of quinones stems from the finding that pyrimidines are efficiently consumed by near-UV photolysis of quinones. Quinones are ubiquitous in nature. They play central roles in aerobic respiration and energy-yielding photosynthesis. Their function is closely related to their redox potentials, which enable them to participate in the transport of electrons within the cell membrane. In addition, exogenous quinones are used as antibiotics and antitumor agents in medicine and hold promise as radiosensitizers in the treatment of cancer. The photoproducts of the reaction with thymine, thymidine and, in part, to 2′-deoxycytidine were identified [10–13]. The initial step in the photooxidation was suggested to be ET from the pyrimidine to the excited quinone. There are some significant reports regarding PET utilizing cytosine, 5-methyl cytosine and cytosine–guanine base pairs [14,15]. Here we have studied the mode of interaction of quinones with C and dC in two different types of media in an effort to elucidate their individual reaction mechanisms. Our studies have revealed that side-by-side with ET, HA between these

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doi:10.1016/j.bpc.2008.11.010

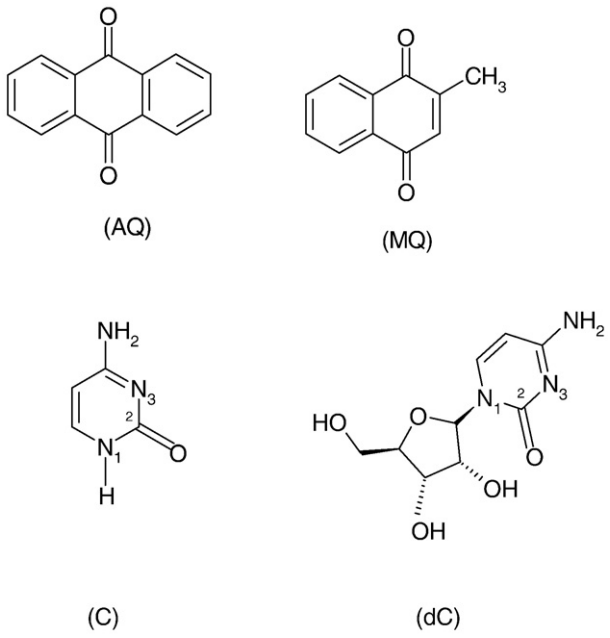


Fig. 1. Structures of molecules used.

molecules are also important. Interestingly, although ET has been discerned with C in both medium we have noticed a drop in its rate with dC in ACN/H_2O so much so that, with change in medium it becomes negligible. In connection to these photochemical effects it is relevant to find out the role of electron transfer in drug–DNA interactions and of the H atom transfer in antioxidant–DNA interaction. In this work, we have mainly focused on this anomalous behavior of C and dC. We hope these studies will be beneficial in predicting the photochemical behavior of the drugs with DNA bases and ultimately with the DNA molecule. Although there have been several reports on quinone–DNA interaction using laser flash photolysis but till now to the best of our knowledge, there has been no report on the effect of medium on the interaction of these molecules with quinones. A study of the medium dependence is important in understanding the effect of environment on the action of a potential drug with biological molecules.

An associated magnetic field effect (MFE) has been utilized in micelles for a better understanding of the reaction intermediates. PET and HA reactions lead to the formation of radical ion pairs (RIPs)/radical pairs (RPs), which contains free electrons and in general can be affected by an external magnetic field (MF) [16–23]. The MFE arises due to competition between electron spin dynamics and radical separation. RPs/RIPs are either generated in singlet or triplet states. The application of an external MF results in Zeeman splitting of the triplet sublevels, which in turn slows down the intersystem crossing (ISC) process thereby increasing the population of the initial spin state. It should be mentioned here that for triplet-derived RPs/RIPs the use of a heterogeneous micellar medium is necessary to observe MFE effects to prolong their lifetime such that they can retain their geminate character for a sufficiently long time for spin flipping to occur [18]. So for a triplet-generated RP, an external MF can increase the triplet population and hence increase radical escape. This is reflected in an increased absorbance and a decreased decay constant on application of MF. Thus the MF can perturb the free radical concentration in a system. This has immense significance in free-radical-based biochemical reactions. MFE has immense potential in identifying the transients formed during reaction, which in turn is useful in the proper elucidation of reaction mechanism. In our system MFE could not be observed in acetonitrile/water (ACN/H_2O, 9:1, v/v) on account of a very short lifetime of transients in such highly polar medium.

Comparison of reaction mechanisms of our system in these two entirely contrasting media has provided some interesting results. In SDS medium the predominant ET mode has been found to get a backseat in comparison to HA which has been attributed to a closer approach of the molecules hence a facile H-bonding among reactant molecules. Again AQ and MQ both have undergone ET and HA with C in both media. With dC a drop in reaction rate has been observed and our study have revealed that to be due to a low ET rate. This change in reactivity of dC has been attributed to the additional ribose unit, which has succeeded in inhibiting a keto-enol tautomerism which generally endows the base unit C with an aromatic nucleus. Changing of media has resulted in a switchover of reactivity of dC only, which is more marked in case of AQ. With dC, ET has been almost quenched to give way to a sole HA in SDS.

2. Experimental

2.1. Materials

Menadione (MQ), cytosine (C), cytidine (dC) and sodium dodecyl sulphate (SDS) were purchased from Sigma. 9,10-anthraquinone (AQ) was obtained from Aldrich and was recrystallised from ethanol. UV spectroscopy grade acetonitrile (ACN) was obtained from Spectrochem and used without further purification. Water used for preparation of solutions was triply distilled. All micellar solutions were made by sonication. Chemical structures of the molecules used in this work are shown in Fig. 1.

2.2. Spectral methods

Transient absorption spectra are measured using nanosecond flash photolysis set-up (Applied Photophysics) containing an Nd:YAG laser (DCR-II, Spectra Physics). The sample is excited by 355 nm laser light (FWHM=8 ns). The analyzing light is from a 250 W Xenon lamp. The laser and analyzing light beams, crossed at right angles, passed through a quartz cell with 1 cm^2 cross-section. A monochromator equipped with an IP28 photo-multiplier is used to analyze transient absorption (Applied Photophysics). The signals from the photo-multiplier are displayed and recorded as a function of time on a Tektronix 500 MHz (1 Gs/s sampling rate) oscilloscope, TDS 3054B and the data has been transferred to a computer using TekVISA software. Each data point has been obtained with multi-times average to improve the signal-to-noise ratio. The transient absorption spectra are obtained from a series of oscilloscope traces measured with the same

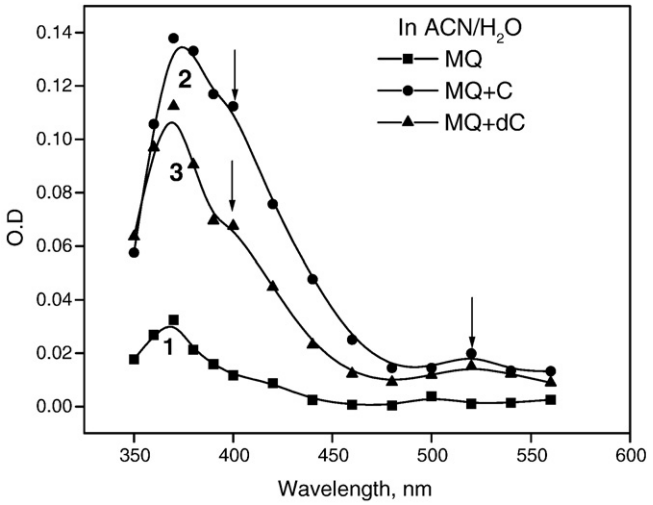


Fig. 2. Transient absorption spectra of (1) MQ (0.4 mM) (■), (2) MQ (0.4 mM)–C (5.0 mM) (●) and (3) MQ (0.4 mM)–dC (5.0 mM) (▲) at 0.8 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

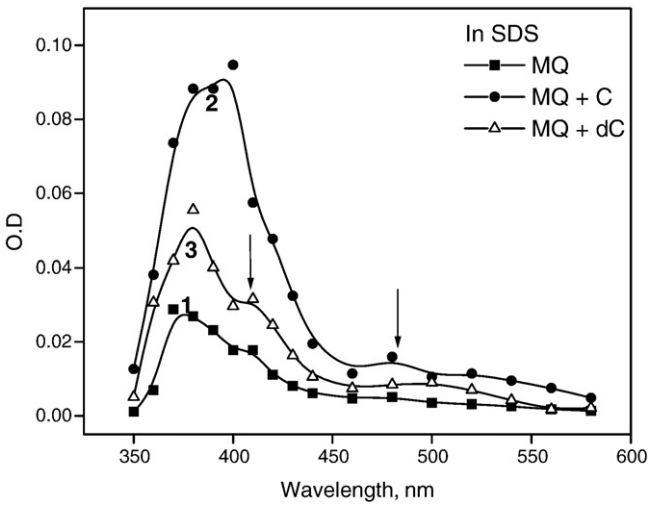


Fig. 3. Transient absorption spectra of (1) MQ (0.4 mM) (■), (2) MQ (0.4 mM)–C (5.0 mM) (●) and (3) MQ (0.4 mM)–dC (5.0 mM) (Δ) at 0.8 μs time delay after laser pulse with excitation wavelength 355 nm in 5% SDS micelles.

solution in a point-by-point manner with respect to the wavelength using the software Origin 5.0. The samples have been deaerated by passing pure Argon gas for 20 min prior to each experiment. No degradation of the samples has been observed during the experiments. The MF effect (0.08 T) on the transient spectra has been studied by passing direct current through a pair of electromagnetic coils placed inside the sample chamber.

2.3. Kinetic analysis of magnetic field effect

In the presence of an external magnetic field, the decay of the radical pair is expected to be biexponential [24] i.e., the following equation is obeyed for the change in absorbance $A(t)$

$$A(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t)$$

where k_f and k_s are the respective rate constants for the fast and slow components of the decay profiles. The fast components of this equation correspond to the radical pair decay in the micellar cage, while the slower one is due to the reaction of the escaped radicals. The relative radical escape yields (Y) of the radical ions in the bulk of the solvent may be obtained from the ratio of the absorption due to the free radical ions to that of the initial absorption immediately after the pulse. We have calculated Y after 5 μs of laser flash.

3. Results

3.1. Interaction of C and dC with MQ

3.1.1. Triplet and radical absorption spectra

The transient optical absorption spectra obtained on irradiating 0.4 mM MQ separately and in the presence of pyrimidine base C (5 mM) and its corresponding nucleoside dC (5 mM) dissolved in ACN/H_2O (9:1, v/v) 0.8 μs after laser flash at 355 nm are displayed in Fig. 2.

Table 1
λ_{max} of different RPs/RIPs

Species	λ_{max} (nm)	Second peak (nm)
$MQH^{\bullet}$	370	410
$MQ^{\bullet-}$	390	480
$C^{\bullet+}$	480–500	
$AQH^{\bullet}$	370	
AQH_2	460	
$AQ^{\bullet-}$	~400	~520

Irradiation of MQ alone generates a peak around 370 nm (curve 1), which has been assigned to triplet–triplet absorption of ^{3}MQ [3]. Addition of C (curve 2) has resulted in a sharp increase in intensity with peak around 370 nm and a hump at 410 nm. The region around 500 nm exhibits another peak. The increased absorption at 370 nm may apparently seem to be due to increased yield of ^{3}MQ upon energy transfer from C. But energy transfer is reported to be very unlikely between quinones and DNA bases [25,26]. So the only possibility is ET. In our earlier works [2–4] we have mentioned that upon ET, MQ serves as an electron acceptor and generates the radical anion $MQ^{\bullet-}$ which absorbs around 390 nm with a second peak around 480 nm. We have also reported that upon irradiation if HA occurs from a suitable H atom donor molecule a semiquinone $MQH^{\bullet}$ is formed, which absorb around 370 nm with a hump at 410 nm. Now C is reported to undergo dehydrogenation/deprotonation [27] on irradiation and there are also some reports on cytosine involved in PET [15,28]. PET from C generates cytosine radical cation ($C^{\bullet+}$), which is reported to absorb around 480–500 nm [7,29]. Curve 2 reveals peak at 370 nm and a second one around 500 nm which indicates the presence of $MQ^{\bullet-}$ and $C^{\bullet+}$ formed through ET. A small shoulder around 400 nm in the spectrum indicates $MQH^{\bullet}$ [2]. It is reported that radical cation of methyl cytosine can undergo rapid deprotonation. So in our case too, ET can be considered to precede H atom transfer. With dC (curve 3) the nature of the spectrum remains almost the same but with a reduced intensity. This reduced intensity at 370 nm can be due to a lower reactivity of dC than C. Cytidine possesses an additional sugar moiety, so we believe that, this sugar unit has somehow hindered a smooth reaction from the base part. HA from sugar unit was reported earlier [30–33]. So a simultaneous ET and HA is also favorable with dC. Having established the reaction pathway between MQ and C/dC in homogeneous medium we have searched for the same in micellar medium. Fig. 3 shows the transient optical absorption spectra obtained on irradiating 0.4 mM MQ separately and in the presence of C (5 mM) and its corresponding nucleoside dC (5 mM) in 5% SDS, 0.8 μs after laser flash. MQ reveals a peak at 370 nm with a hump at 410 nm (curve 1), which is characteristic of $MQH^{\bullet}$ formed upon uptake of H from a nearby SDS molecule [34]. The spectrum due to C (curve 2) has a maximum around 400 nm with appreciable absorption around 480 nm. This suggests existence of radical ion pairs ($C^{\bullet+}$ and $MQ^{\bullet-}$) and also $MQH^{\bullet}$. Coexistence of $MQ^{\bullet-}$ and $MQH^{\bullet}$ in equal proportion is evident from a broad peak around 380–400 nm with a small peak ~480 nm [3]. So in SDS medium also, ET and HA are evident between C and MQ. In case of dC, the peak height decreases around 390 nm but the 410 nm hump becomes more prominent than that with C. Now

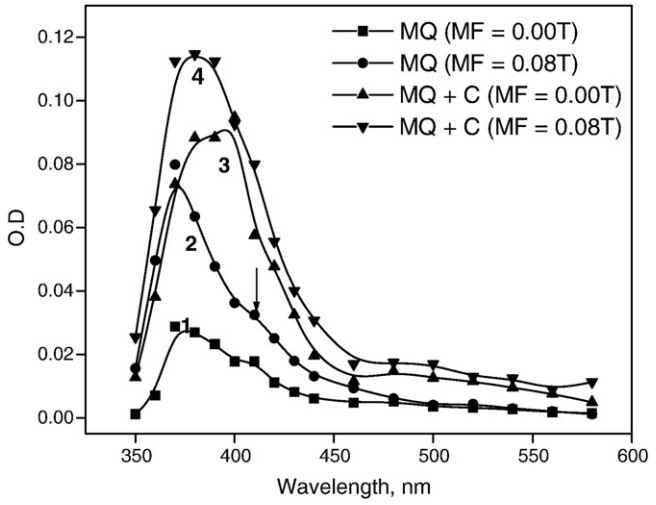


Fig. 4. Transient absorption spectra of MQ (0.4 mM) (1) in the absence (■) and (2) presence of magnetic field (●), MQ (0.4 mM)–C (5.0 mM) in the (3) absence (▲) and (4) presence of magnetic field (▼) at a delay of 0.8 μs in SDS micelles.

$MQH^{\bullet}$ absorbs around 370 nm with a hump at 410 nm and $MQ^{\bullet-}$ absorbs mainly around 380–400 nm with a small peak at 480 nm. The λ_{max} of different RPs/RIPs are given in Table 1. So in comparing curves 2 and 3 of Fig. 3, it is clear that dC exhibits a much more prominent hump at 410 nm than C. So HA is found to gain predominance over ET in case of dC upon medium change to SDS.

3.1.2. Magnetic field effect

A confirmatory support for the existence of RPs and RIPs comes from an observation of MFE with the bases in SDS medium. Fig. 4 shows the transient optical absorption spectra obtained on irradiating 0.4 mM MQ separately and in the presence of C (5 mM) in the presence of an external MF, 0.8 μs after laser flash. Curve 2 reveals the effect on application of an external MF on MQ where an increase in the 370 nm peak and the 410 nm hump can be discerned. The formation of a spin correlated radical pair ($^3MQH^{\bullet\bullet}R$) (reaction 2) explains this MFE (reaction 3). On addition of C (curve 3) a broad spectrum is generated with a maximum around 390 nm with a hump above 480 nm. Field effect on the MQ–C interaction shows some interesting behavior. The increment at 380 nm on application of field is much prominent than the 480 nm region. Now $MQH^{\bullet}$ and $MQ^{\bullet-}$ are both responsible for the 380 nm peak while the 480–500 nm regions are the signatures of $MQ^{\bullet-}$ and cytosine radical cation ($C^{\bullet+}$) generated upon ET. The most important criterion of observing MFE in SDS is the geminate behavior of RPs/RIPs. So it is evident that semiquinone ($MQH^{\bullet}$) formed upon HA remains geminate within the time interval when spin and diffusion dynamics operate to exhibit observable MFE. While the RIPs generated on ET must be present in lower concentration than $MQH^{\bullet}$ and probably loses their geminate character soon. Low MFE does not rule out the existence of RIPs since some absorption is still present above 480 nm (Fig. 4, curve 3). Hence HA is found to be somewhat more important than ET in SDS medium with C.

Fig. 5 illustrates the spectra obtained on irradiating MQ separately and in the presence of dC (5 mM) in the presence of an external MF. Addition of dC generates a spectrum (curve 3) which is almost similar to the one due to MQ alone (curve 1) except a small hump at 500 nm. But this spectrum is much different from the one due to C. So it is evident that, dC has produced predominantly $MQH^{\bullet}$ in SDS while C has produced both $MQH^{\bullet}$ and $MQ^{\bullet-}$. Similar to our observations in homogeneous medium, dC has exhibited a lower reactivity than C in micellar medium too. So this can only be due to their structural difference. Hence a study of MFE confirms that C supports both ET and HA while dC supports mainly the latter. In this context it is necessary to

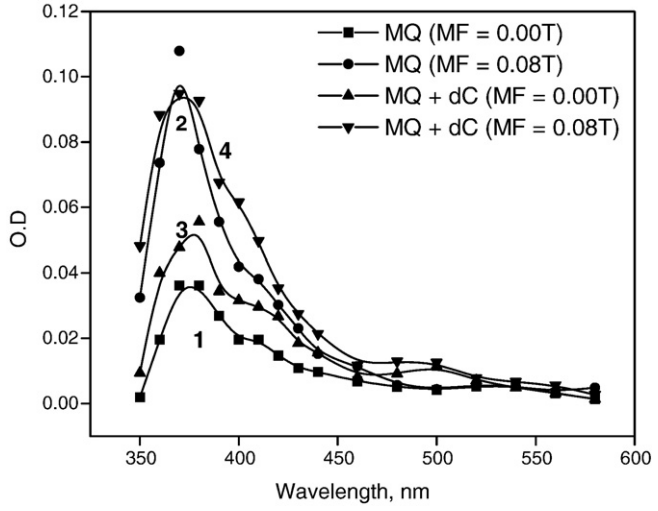


Fig. 5. Transient absorption spectra of MQ (0.4 mM) (1) in the absence (■) and (2) presence of magnetic field (●), MQ (0.4 mM)–dC (5.0 mM) in the (3) absence (▲) and (4) presence of magnetic field (▼) at a delay of 0.8 μs in SDS micelles.

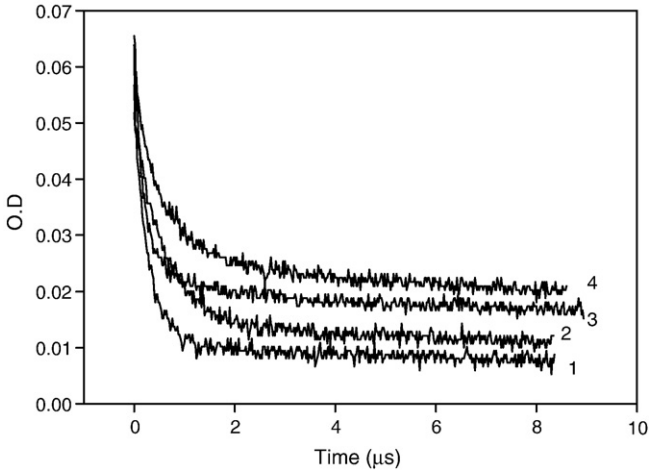


Fig. 6. Normalized OD traces at 380 nm obtained by laser flash photolysis (λ = 355 nm) of MQ (0.4 mM) in SDS in the (1) absence and (2) presence of magnetic field, MQ (0.4 mM) and C (5.0 mM) in the (3) absence and (4) presence of magnetic field.

mention that $MQH^{\bullet}$ is also produced upon H uptake from SDS molecule. But the role of C/dC in H donation has been proved by a further increase in 370 nm peak over that of curve 1 in both Figs. 4 and 5.

3.1.3. Kinetic analysis of magnetic field effect

A further support of the reaction mechanism is provided by kinetic analysis of decay curves. Fig. 6 reveals the normalized absorbance traces at 380 nm by laser flash photolysis of MQ and MQ–C in the absence and presence of MF. In the presence of an external magnetic field, the decay of the transient at 370 nm becomes slower (Fig. 6) accompanied by an enhanced absorption in the spectrum (Fig. 4). The formation of a spin correlated RP being responsible for this MFE. It is noteworthy that the nature of the decay profiles is different in the presence of C particularly in the presence of a MF. This implies that the RPs/RIPs formed with C are also different from the one produced with MQ alone. MQ in SDS alone can generate only $MQH^{\bullet}$ on H atom transfer. Since C has behaved somewhat differently so we can confirm, along with $MQH^{\bullet}$, some RIPs must be present [3]. A chance of indirect H atom transfer from C through SDS is also possible.

$$R^{\bullet} + C \rightarrow RH(SDS) + C(-H)^{\bullet}. \quad (1)$$

But such indirect formation will generate $C(-H)^{\bullet}$ which would have no spin correlation with $MQH^{\bullet}$. This would quench the MFE. So observation of MFE is a proof of direct ET and H atom transfer from C/dC to quinones. Table 2 depicts the decay rate constant (k_f) and relative radical escape yield (Y) after 5 μs for MQ with the bases. From Table 2, it is observed that with increasing field, the decay rate decreases and simultaneously the relative radical escape yield increases. This implies that RIPs are formed as intermediates with an initial triplet spin state. Upon application of a magnetic field, the conversion of the triplet RIP to the singlet RIP is retarded, and consequently, the decay rates are

Table 2
Variation of decay rate constant (k_f) and relative radical escape yield (Y) with magnetic field for aqueous micellar solution (SDS) of MQ and the bases

Base	Magnetic field (T)	Decay rate Constant (k_f) $(s)^{-1}$	Y
No base	0.00	4.63×10^6 (±0.02)	1.00[a]
	0.08	1.58×10^6 (±0.01)	1.28
C	0.00	5.95×10^6 (±0.03)	1.00[a]
	0.08	4.05×10^6 (±0.05)	1.50
dC	0.00	4.84×10^6 (±0.03)	1.00[a]
	0.08	3.91×10^6 (±0.01)	1.22

[a] Arbitrarily taken.

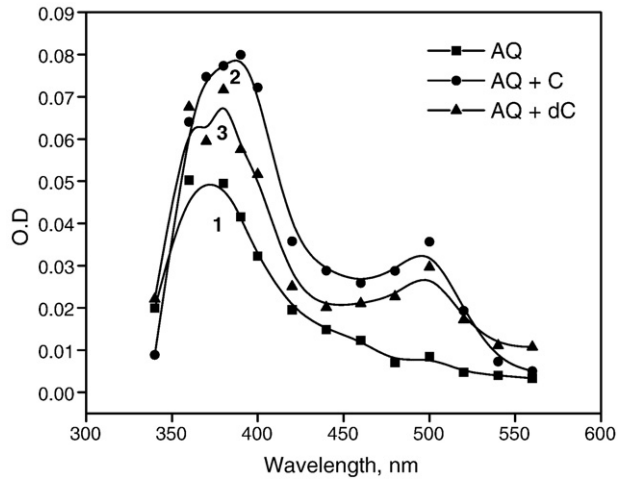


Fig. 7. Transient absorption spectra of (1) AQ (0.4 mM) (■), (2) AQ (0.4 mM)–C (5.0 mM) (●), (3) AQ (0.4 mM)–dC (5.0 mM) (▲) at 0.8 s time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

decreased and escape yield of the radicals is increased. Thus observation of MFE at this wavelength is a convincing proof of the existence of RPs/RIPs thus substantiating our theory.

3.2. Interaction of C and dC with AQ

3.2.1. Triplet and radical absorption spectra

AQ differs from MQ in having an extra phenyl group. So next we have conducted our experiments with AQ to find if increased size can affect the reaction course. Fig. 7 displays transient absorption spectra upon irradiation of a 0.4 mM AQ solution separately and in the presence of 5 mM C and dC after 0.8 μs of laser flash in ACN/H_2O. AQ alone presents strong maxima around 360 nm, which is due to triplet absorption of ^{3}AQ [1]. Additions of DNA bases lead to an increase in absorption around 360–380 nm regions with another peak at 500 nm. We have reported earlier AQ radical anion ($AQ^{\bullet-}$) absorbs around 390–400 nm with a second peak around 540 nm in pure acetonitrile medium [1]. So the 500 nm hump can be well associated to the second peak of $AQ^{\bullet-}$. The blue shift can be attributed to a solvent effect. On comparison with MQ in Fig. 2, we have found an interesting observation. Spectra of MQ possess a small 480 nm peak while AQ is seen to have a well-defined 500 nm peak. We think, this is due to a higher RIP concentration is case of AQ. A higher radical ion concentration is an indication of a better ET in AQ. So why does AQ support ET better than MQ? Electron transfer depends on the ionization potential of the donor and the electron affinity (EA) of the acceptor [35]. So by varying the acceptor, AQ and MQ as in our case, if EA can be varied, extent of ET can also be affected. AQ is reported to possess a higher EA than MQ [36,37]. So AQ is expected to display a better ET, which is indeed the case. $AQH^{\bullet}$ absorbs very close to that of $AQ^{\bullet-}$ (~370 nm) [1] and thus it is extremely difficult to confirm its presence in ACN/H_2O. A prominent 500 nm peak indicates a prominent ET in this medium while HA can be considered to be almost negligible.

3.2.2. Magnetic field effect

We have repeated our experiments in 10% SDS to find whether AQ still maintains a dominant ET chemistry here. Fig. 8 displays the transient absorption spectra obtained on irradiating AQ separately and in the presence of C (5 mM) in the presence of an external MF. Curves 1 and 2 exhibit the transient absorptions due to AQ in the absence and presence of MF. Application of MF has resulted in an increase in absorbance around 370 nm, which is attributed to the presence of the AQ semiquinone, $AQH^{\bullet}$ formed upon HA from a SDS molecule [1]. There is a broad band around 460 nm, which remains unchanged on application of field. This has been associated to the formation of a non-radical species AQH_2, formed upon two simultaneous H atom transfer to AQ [1].

$$^3AQ^* + H^{\bullet} \rightarrow AQH^{\bullet}$$

$$AQH^{\bullet} + H^{\bullet} \rightarrow AQH_2$$

Curve 3 reveals the behavior in the presence of C. It possesses a broad peak at 360–390 nm region which seems to be generated upon superposition of two peaks, ~370 nm and ~400 nm. This can only be explained by the simultaneous existence of $AQH^{\bullet}$, with λ_{max} ~370 nm and $AQ^{\bullet-}$ with λ_{max} ~390–400 nm. Presence of appreciable field effect in the same regions is a further proof for their existence. The peak due to $C^{\bullet+}$ is probably masked by the AQH_2 one. So both ET and HA are found to be operative. But an interesting difference is found with dC. Fig. 9 displays the transient absorption spectra obtained on irradiating AQ separately and in the presence of dC (5 mM) in the presence of an external MF. Here again curves 1 and 2 exhibit the transient absorptions due to AQ alone in the absence and presence of MF while curves 3 and 4 reveal the behavior in the presence of dC.

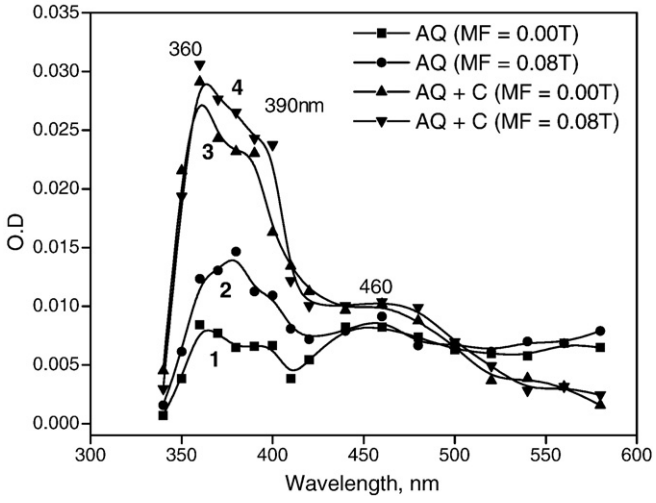


Fig. 8. Transient absorption spectra of AQ (0.1 mM) (1) in the absence (■) and (2) presence of magnetic field (●), AQ (0.1 mM)–C (5.0 mM) in the (3) absence (▲) and (4) presence of magnetic field (▼), at a delay of 0.8 s in SDS micelles.

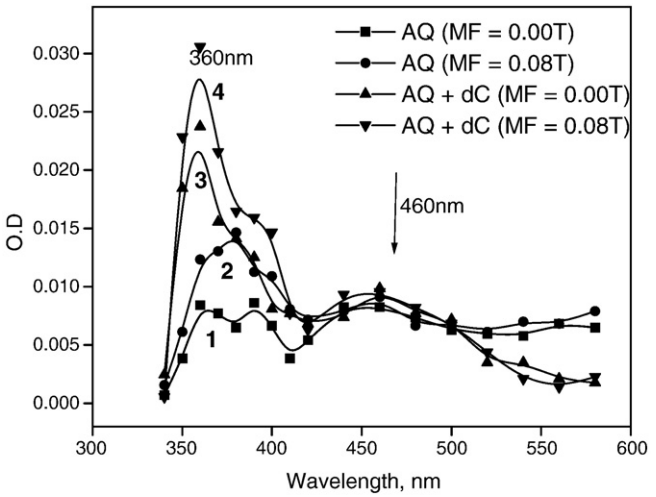


Fig. 9. Transient absorption spectra of AQ (0.1 mM) (1) in the absence (■) and (2) presence of magnetic field (●), AQ (0.1 mM)–dC (5.0 mM) in the (3) absence (▲) and (4) presence of magnetic field (▼), at a delay of 0.8 s in SDS micelles.

Table 3
Variation of decay rate constant (k_f) and relative radical escape yield (Y) with magnetic field for aqueous micellar solution (SDS) of AQ and the bases

Base	Magnetic field (T)	Decay rate constant (k_f) $(s)^{-1}$	Y
No base	0.00	3.15×10^6 (±0.02)	1.00[a]
	0.08	1.56×10^6 (±0.01)	1.25
C	0.00	4.54×10^6 (±0.03)	1.00[a]
	0.08	1.73×10^6 (±0.05)	1.27
dC	0.00	4.59×10^6 (±0.03)	1.00[a]
	0.08	2.25×10^6 (±0.01)	1.43

[a] Arbitrarily taken.

Curve 3 of Fig. 9, due to AQ–dC interaction, shows a much sharper peak with a maximum at 370 nm with a very small 400 nm hump. There is an appreciable MFE around these regions. This behavior is attributed to the presence of a very high concentration of $AQH^{\bullet}$ in comparison to $AQ^{\bullet-}$ in the presence of dC. Thus a dominant HA is evident in SDS medium. These observations point to a weaker ET in case dC in SDS. Thus we find, with AQ, the dominant ET chemistry is operative with C but not with dC in SDS.

3.2.3. Kinetic analysis of magnetic field effect

Similarly as MQ, we have calculated the decay rate constant and radical escape yield for AQ with the bases with similar decay curves (graph not shown). Table 3 reveals the decay rate constant (k_f) and relative radical escape yield (Y) values for AQ with the bases. Similar to MQ it is observed that with increasing field, the decay rate decreases and correspondingly the escape yield increases. So an initial triplet spin state for AQ is also confirmed. Thus MFE establishes the triplet spin state for ET and HA with both the quinones.

4. Discussion

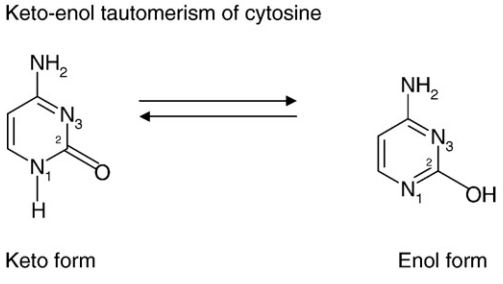
Now several intriguing features are evident from the results. Firstly, a predominance of HA in SDS medium has been discerned in case of both quinones with the bases. Actually in SDS, molecules are closely sequestered [38,39] which results in less chaotic movement of these molecules. Again the possibility of remaining at a close proximity is higher [2–4]. We presume a H bonding type interaction precedes HA. There are also some indirect evidence of H bond formation between quinones and DNA bases [40,41]. Thus closer approach among molecules enhances the probability of H bonding and thus the scope of HA is also enhanced. Similar phenomenon of H bonding is not possible in ACN/H_2O so probability of HA decreases. It is well known that two molecules forming an H bond in a less polar environment loses the strength of H bonding in an aqueous medium [42]. In aqueous solution, the solvent–MQ and solvent–base interactions predominate, and H bonding with the solvent is favored. Therefore, H atom transfer is not significant in water. The solvent acetonitrile is also polar where dipole–dipole interactions with MQ and bases exist. This may reduce the possibility of H bonding between them. The micelle not only provides the non-polar environment but also enhances the local concentration of MQ and bases in its interior. It is quite plausible that the higher concentration makes possible the H bonding interaction and H atom transfer. In other words, the micellar environment forces MQ and bases to form H bond which breaks in polar and homogeneous environments due to solvent interaction and dilution. So SDS has an intrinsic tendency to favor HA. HA, if any, found in ACN/H_2O depend on the strong H donor ability of reactants.

Secondly, a lower reactivity of dC in comparison to C has been discerned in both homogeneous and heterogeneous media. Sugar moiety due to its hydroxyl groups undergoes facile HA thus dC as a whole will favor HA. Again increased size of dC will keep MQ at a further distance than C. This may hamper ET from the base part, but perhaps the most important factor is tautomerism. Keto-enol tautomerism is reported to have a significant role in the chemistry of cytosine [43,44]. Cytosine can undergo keto-enol tautomerism and the enol form possesses an aromatic benzene nucleus as shown in Scheme 1. Cytidine possesses an extra ribose unit at N1 position so the tautomerism, is no more possible. It is possible that in equilibrium sufficient amount of the enol form of cytosine exists. This enol form is susceptible to facile ET to MQ. Now in dC absence of this enol form is expected to reduce the ET rate. Hence dC in effect will have a lower reactivity than C and will encourage HA more.

Thirdly, comparing the behavior of both C and dC with quinones in both media, we find, behavior of C remains almost unchanged. On the other hand, dC has made an interesting switchover from predominant ET in ACN/H_2O to a predominant HA in SDS with AQ. Now AQ possesses a higher EA, which would entitle it with a favorable ET chemistry. But in SDS this ET is found to be unfavorable only with dC and not C. This can be attributed partly to a medium effect and partly to a structural effect. C is intrinsically rich in electron density due to electron delocalization from amino moiety [45] and if we assume the keto-enol tautomerism, the enol tautomer (Scheme 1) possesses an aromatic sextet. So C has a higher probability of transferring electrons during ET. In ACN/H_2O, competitive reaction like HA is not significant while in SDS it is. But still, a higher tendency of transferring electrons has favored ET from C even in SDS. But dC, the nucleoside, shows a different behavior. The lower rate of reaction, specifically ET, has been attributed to a failure in attaining aromaticity by keto-enol tautomerism. Again Steenken has reported that the electron withdrawing inductive effect of sugar moiety is also somewhat responsible for decreasing ET in dC [46]. Cytidine contains several H donor moieties, namely the $-NH_2$ moiety and the sugar unit thus HA will be more important than ET. But in ACN/H_2O due to failure of H bonding among molecules, probability of HA is less. As a net result, dC in ACN/H_2O possesses a low reaction rate than C while in SDS it undergoes a complete switchover from ET to HA. We have already mentioned how SDS promotes HA on account of a favorable H bonding between molecules. Since dC possesses good H donor centers it can suitably H bond to quinone moieties. This possibility in conjunction with a weaker tendency of dC to participate in ET helps in the complete switchover of reaction from a dominant ET in ACN/H_2O to HA in micelles. Similar phenomenon is not found with C where H donating centers are less coupled with a good electron donating capability. So we find, environment acts as an excellent means in controlling reaction pathways among similar group of molecules.

5. Conclusion

We have demonstrated the differential behavior of C and its nucleoside dC with two quinones of different size, MQ and AQ. There has been a change in reactivity on changing molecular structure of the bases and medium change. ET and HA have been found to occur with C with AQ and MQ in ACN/H_2O and SDS. But with dC, there has been a fall in ET in comparison to C due to tautomerism. But still, AQ has supported a better ET with dC in comparison to that with MQ due to a higher EA, in ACN/H_2O, and interestingly, on changing medium, the ET



Scheme 1. Keto-enol tautomerism of cytosine.

from dC gets completely replaced by H transfer. This has been explained on the basis of structural difference of dC from C and an effect of micellar medium in favoring H transfer.

Acknowledgements

We sincerely thank Mrs. Chitra Raha and Mr. Tapan Pyne for their kind assistance and technical support.

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